

Characterization of Carbon in Fly Ash Using Controlled-Atmosphere Programmed-Temperature Oxidation (CAPTO)

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SUMMARY

INTRODUCTION

The high volume of Coal Combustion By-Products (CCBs) produced on a yearly basis prompted the American Coal Ash Association to establish an International Symposium, and through technology transfer, to promote the use of CCBs over a wide range of markets. The 114 presentations at the 12th International Symposium on CCBs¹, establishment of the Unburned Carbonaceous Material on Utility Fly Ash Conference², and recent symposia at national scientific meetings³ provide ample evidence of the strong continuing interest in commercial applications for CCB's. A recent report reviews markets, physical and chemical characteristics, classification and specifications, and quality control related to pulverized coal ash⁴.

FLY ASH CHARACTERIZATION

Several recent studies, using a variety of techniques, have characterized fly ash⁵ including the unburned carbon content⁶. The use of low NO_x burners on coal fired boilers, in numerous instances, has resulted in either an increase of unburned carbon in fly ash or more variation in its carbon content. This variation or increased carbon content directly impacts the sale of fly ash used with cement to produce concrete products. A number of methods for rapid measurement of the carbon content in fly ash are available or under study². Even when fly ash meets loss on ignition (LOI) specifications, variation in the adsorption properties of the carbon forms present may result in variation of the amount of surfactants required for use as air entrainment agents⁷. A further study to characterize the behavior of soot and carbon black with air entrainment surfactants has been reported⁸.

This controlled-atmosphere programmed-temperature oxidation (CAPTO) study centers primarily on thermal characterization of the carbon forms present in fly ash samples obtained from several different sources. The characterization of carbon forms in fly ash is fundamental to understanding the behavior of air entrainment surfactants with unburned carbon in fly ash/cement mixtures. These studies may also lead to prediction of surfactant performance thus minimizing variability in concrete products. Additionally, a correlation between power plant operating conditions or coal blend and one or more unburned carbon forms present in fly ash may exist. Continuing studies using CAPTO for characterization of coal blend-fly ash pairs, in conjunction with other characterization studies, may lead to a better prediction of total and

forms of unburned carbon present in fly ash. Furthermore, these characterizations may suggest routes for minimizing total unburned carbon or specific forms of unburned carbon in fly ash.

CHARACTERIZATIONS USING CAPTO

The patented CAPTO method has been used to characterize the carbon, hydrogen, and sulfur forms present in coals, activated carbon, and numerous organic/inorganic mixtures^{9,10,11}. The system was originally conceived and effectively used for analysis of treated coals many of which did not respond well to classical coal analysis methods after treatment.

Previous work has shown that coal samples dispersed in a diluent/oxidation catalyst and subjected simultaneously to a plug flow oxygen/inert gas stream and a linear increase in temperature evolve CO₂, H₂O, SO₂, and NO₂ intermittently as a function of temperature. A secondary furnace held at an elevated temperature is used to insure constant SO₂ - SO₃ equilibrium conditions and that all gases produced at any oxidation temperature enter infrared gas cells for analysis at the same temperature. Distinctive H₂O, CO₂ and SO₂ evolution patterns (Figure 1) are observed for coals of different rank and between raw and treated coals. Each gaseous oxide evolution is quantitatively measured and related to the structural entity producing the evolution. For example, SO₂ evolutions (Figure 2) are related to elemental sulfur, non-aromatic organic sulfur, aromatic organic sulfur, pyritic sulfur, and sulfatic sulfur (jarosite and sulfate) structures in coal^{12,13}. Integration of all SO₂ evolution peaks from untreated coals resulted in total and sulfur forms values in good agreement with those obtained by ASTM methods¹². Continued research and development resulted in a one-step method for the direct determination of the inorganic and organic carbon, hydrogen, and sulfur forms in coal and more efficient instrumentation for the analysis¹³.

CAPTO (Figure 3) is most similar to thermal gravimetric analysis-Fourier transform infrared (TGA-FTIR) evolved gas analysis instrumentation. However, important differences exist. In a TGA experiment which uses a significant sample size, much of the gas flow is around the sample. The sample is not uniformly exposed to the oxidant and the evolved gases at a given temperature are not representative of the entire sample. Exotherms may occur leading to significant loss of peak resolution. If a very small sample is used to minimize these effects, a mass spectrometer is required even for semi-quantitative analysis.

CAPTO utilizes (1) a 50 - 200 mg sample, (2) an inert diluent (with high diluent:sample ratio) to promote selective oxidation and avoid exotherms, (3) oxidant plug-flow through the sample ensures uniform oxidation. These features coupled with a furnace design to minimize temperature variation across the sample zone and a secondary furnace to ensure that all gases enter the analysis cells at the same temperature/equilibrium conditions, result in well resolved FTIR absorbance/temperature profiles.

RESULTS

Using CAPTO, forms of carbon and other elements present in the unburned carbon of fly ash were characterized. A series of fly ash samples obtained from several different power stations burning pulverized coal were studied (Table 1). Nearly all of the fly ash samples characterized (Figure 4) showed

carbon oxidation in four different temperature ranges (Tables 2 and 3). Three of these temperature ranges are well above those of coals (Figure 5), activated carbon, and other chars and significantly below the oxidation temperature of graphite (Figure 6). The amount of carbon dioxide evolving in each temperature range has been evaluated (Tables 2 and 3).

Fly ash sample #9 resulted from a combustion stream injected with activated carbon. The CAPTO profile shows the presence of activated carbon in addition to the carbon forms noted above (Figure 7). Clearly, the CAPTO characterization method provides a route to distinguish among coal or char carbon accumulating in the fly ash. Sample #9 has an elevated sulfur content in comparison to the other fly ash samples and the sulfur values have been reported in Tables 4 and 5.

CONCLUSIONS

- The major portion of unburned carbon in the fly ash samples oxidizes in CAPTO at temperatures distinct from those of coal, activated carbon, and graphite.
- A few percent of unburned carbon in the fly ash samples oxidizes in the temperature range normally associated with CAPTO oxidation of non-aromatic coal structures.
- Evolution of CO₂ at four different temperature ranges for most of the fly ash samples suggest that at least four distinct forms of carbon are detectable using controlled oxidation conditions.
- Fly ash samples from different sources show variation in the amount of CO₂ evolved at each of three major evolution temperature regions suggesting variation in the amount of carbon forms among the fly ash samples characterized.
- One fly ash sample produced during evaluation of injected activated carbon clearly shows that the CAPTO method can be used to distinguish the unburned carbon forms from activated carbon and other "coal like" carbons present in the fly ash.

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REFERENCES

1. American Coal Ash Association and Electric Power Research Institute, Proceedings: 12th International Symposium on CCB Management and Use, Volume 1-3, January 26-30, 1997.

2. Pittsburgh Energy Technology Center, U.S. Department of Energy, Proceedings: Second Conference on Unburned Carbonaceous Material on Utility Fly Ash, March 5-6, 1996.
3. American Chemical Society 211th National Meeting, Am. Chem. Div. Fuel Chem. Prepr. 1996, 41(2), 553-694.
4. Sloss, L.L, Smith, I.M, Adams, D.M.B., "Pulverised coal ash - requirements for utilisation", Report Number IEACR/88, IEA Coal Research, London, 1996.
5. Hower, J.C., Robertson, J.D., Thomas, G.A., Wong, A.S., Schram, W.H., Graham, U.M., Rathbone, R.F., and Robl, T.L., "Characterization of Fly Ash from Kentucky Power Plants", Fuel, 75, 403, 1996.
6. Hurt, R.H., Yang, N.Y.C., "Fundamental Characterization of Residual Carbon in Boiler Fly Ash", Proceedings: PETC, USDOE Unburned Carbonaceous Material on Utility Fly Ash Conference, 53, (1995).
7. Freeman, E., Gao, Y.M., Hurt, R., Suuberg, E., Calvert, P., "Interactions of Carbon-Containing Fly Ash with Commercial Air-Entraining Admixtures for Concrete", Proceedings: PETC, USDOE Second Conference on Unburned Carbonaceous Materials on Utility Fly Ash, 27, (1996).
8. Gao, Y.M., Shim, H.S., Hurt, R.H., Suuberg, E.M., Yang, N.Y.C., "Effects of Carbon on Air Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black", Energy & Fuels, 11, 457 (1997).
9. LaCount, R.B., Kern, D.G., King, W.P., LaCount, Jr., R.B., Miltz, Jr., D.J., Stewart, A.L., Trulli, T.K., Walker, D.K., "Advances in Coal Characterization by Programmed-Temperature Oxidation", Fuel, 72, 1203, 1993.
10. LaCount, R.B., King, W.P., Kern, D.G., Walker, D.K., "Determination of Adsorbates Using Programmed Temperature Oxidation (CAPTO)", Proceedings: The 4th Annual International Activated Carbon Conference (IACC), September, 11-12, 1996.
11. LaCount, R.B., Kern, D.G., King, W.P., LaCount, Jr., R.B., Walker, D.K., "Metal Sulfide Content of Ore Samples Determined by Controlled-Atmosphere Programmed-Temperature Oxidation (CAPTO)", Proceedings, Third International Biohydrometallurgy Conference, Vol. I, 665, (1993).
12. LaCount, R.B., Anderson, R.A., Friedman, S., Blaustein, B.D., "Sulfur in Coal by Programmed Temperature Oxidation", Fuel, 66, 909 (1987).
13. LaCount, R.B., Kern, D.G., King, W.P., LaCount, Jr., R.B., Schroyer, T.J., Walker, D.K., "Characterization of Argonne Premium Coals and Treated Coals by Controlled-Atmosphere Programmed-

Temperature Oxidation (CAPTO)", Proceedings: Tenth Annual Pittsburgh Coal Conference, 1159, September, 1993.

Figure 1

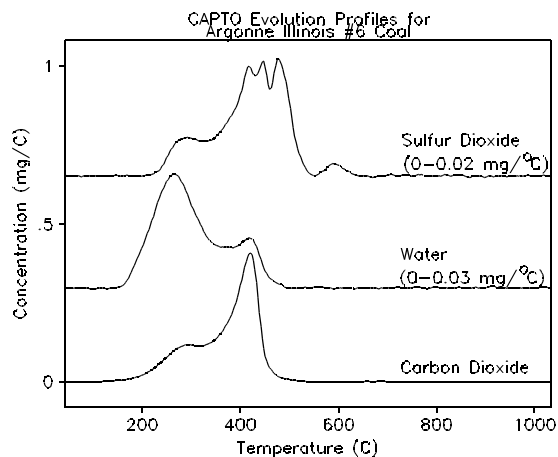


Figure 2

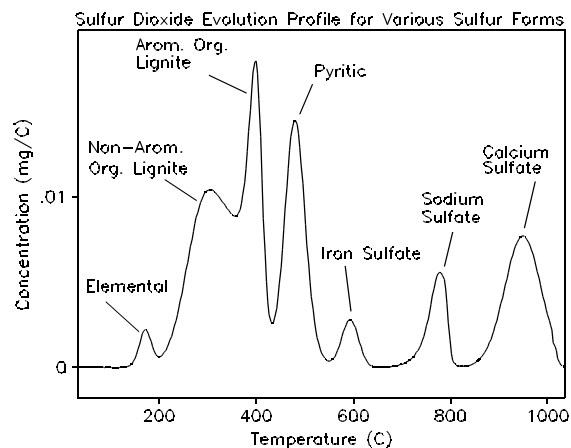
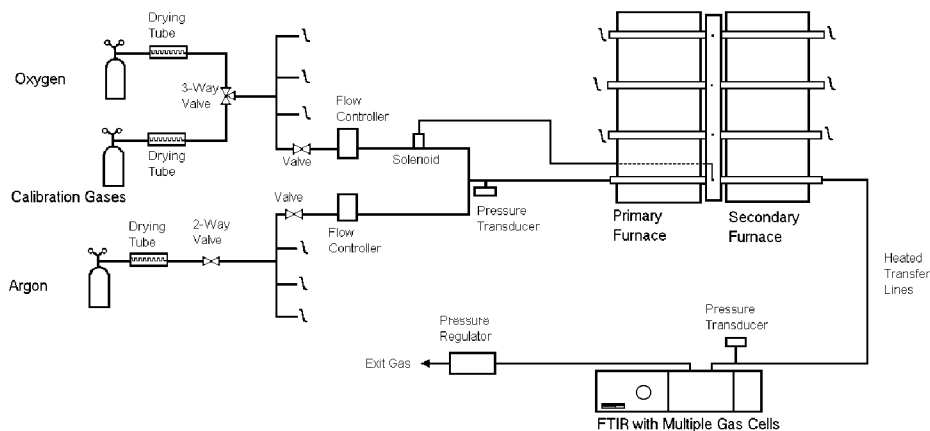


Figure 3



Flow System For Multiple Sample, Controlled-
Atmosphere Programmed Temperature
Oxidation (CAPTO) Apparatus

Figure 5

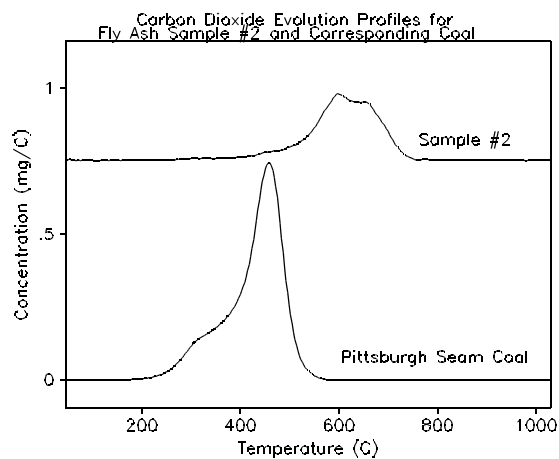


Figure 6

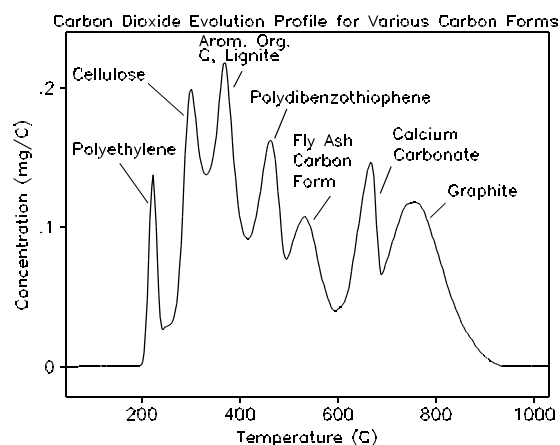


Figure 7

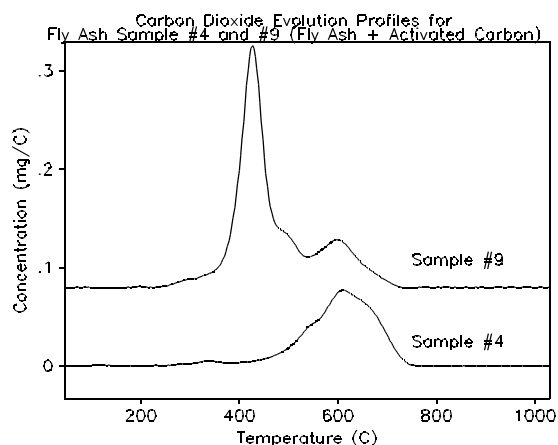
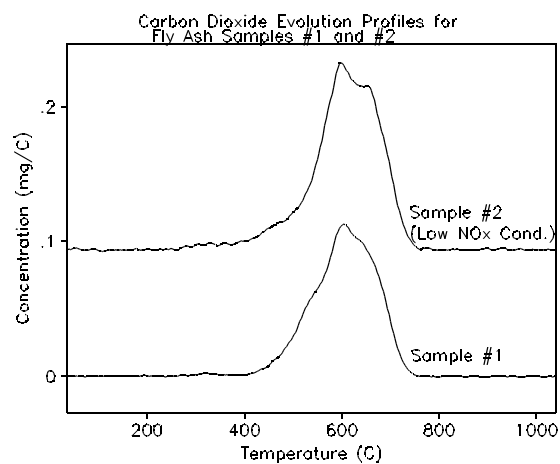


TABLE 1: FLY ASH SAMPLES

Fly Ash	Coal	%C	Burner type	Low NOx
1	Pgh Seam	4.64	Cell Design	No
2	Pgh Seam	3.68	Cell Design	Yes
3	Blacksville	11.14	Wall Fired PC	No
4	Blacksville	5.01	-----	No
5	Appal. Coal	10.60	Wall Fired PC	Yes

Figure 4



6	Bit. Appal. Coal	10.96	Wall Fired PC	Yes
7	Appal. Coal	9.60	Wall Fired PC	Yes
8	East. Ky.	9.38	Wall Fired PC	Yes
9	Fly Ash#4+ Activated Carbon	11.10	-----	No

TABLE 2: CARBON FORMS FOR FLY ASH SAMPLES

(Percent values are relative to Total C)

Sample #	Peak #1	Peak #2	Peak #3	Peak#4
1	319°C (1.08%)	571°C (55.20%)	603°C (12.33%)	661°C (31.37%)
2	319°C (1.76%)	506°C (16.73%)	596°C (47.06%)	667°C (34.43%)
3	319°C (1.99%)	508°C (53.63%)	565°C (44.36%)	-----
4	339°C (3.62%)	542°C (27.75%)	621°C (56.64%)	683°C (11.98%)
5	319°C (1.99%)	501°C (26.40%)	576°C (60.89%)	648°C (10.70%)
6	366°C (1.26%)	517°C (30.12%)	590°C (49.46%)	645°C (19.16%)
7	319°C (2.99%)	449°C (33.20%)	564°C (59.08%)	635°C (4.71%)
8	319°C (2.02%)	506°C (23.53%)	595°C (68.00%)	669°C (6.44%)

TABLE 3: CARBON FORMS FOR FLY ASH SAMPLES #4 AND #9

Sample #	Peak #1	Peak #2	Peak #3	Peak #4	Peak #5	Peak #6
4	339°C (3.62%)	-----	-----	542°C (27.75%)	621°C (56.64%)	683°C (11.98%)
9(Fly Ash #4 + Activated Carbon)	330°C (4.19%)	425°C (50.96%)	486°C (25.27%)	542°C (> 0.01%)	598°C (15.59)	663°C (3.97%)

**TABLE 4: TOTAL CARBON, SULFUR AND HYDROGEN FOR FLY ASH
SAMPLES #4 AND #9**

Sample #	% C	% S	% H
4	5.22	0.22	0.08
9 (Fly Ash #4 + Activated Carbon)	11.10	4.13	0.44

TABLE 5: SULFUR FORMS FOR FLY ASH SAMPLES #4 AND #9

Sample #	Peak #1	Peak #2	Peak #3	Peak #4	Peak #5
4	-----	-----	517°C (33.54%)	609°C (9.66%)	1024°C (56.79%)
9 (Fly Ash #4 + Activated Carbon)	243°C (28.78%)	410°C (9.90%)	598°C (23.44%)	776°C (12.17%)	1003°C (25.70%)